STUDY ON HYDRODESULFURIZATION OF HYDROCRACKED PITCH FROM ATHABASKA BITUMEN. FURTHER TEST OF THE MICROWAVE PROCESS

FINAL REPORT

BY

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CONTENTS

Page

INTRODUCTION 3

EXPERIMENTAL 4

1. The microwave radiation sources 4

   (a) The design and construction of an X-band resonant cavity system for high intensity microwave irradiation of chemicals 4
   (b) The use of a low-power commercial microwave oven as the microwave source 5

2. The analytical methods 6

   (a) Sulfur analysis 6
   (b) Gas chromatography 7
   (c) Mass spectrometric analysis 7
   (d) On-line Gc/Mass spectrometer 7
   (e) Preparation of metal hydrides 8

RESULTS AND DISCUSSIONS 9

1. Hydrodesulfurization of pitch with metal powder and conventional hydride with 2 kW microwave irradiation 9

2. Hydrodesulfurization of pitch with metal hydride powder and microwave radiation 12

3. Investigation of the gaseous products in the microwave metal hydride hydrodesulfurization of pitch 14

4. Preliminary experiments on microwave hydrodesulfurization of other organic materials 16

5. Preliminary experiments using the cavity based X-band microwave system 16

6. Preliminary estimate of the energy balance in the microwave hydrodesulfurization processes 18

CONCLUSIONS AND SUGGESTIONS 19

INTRODUCTION

In order to achieve maximum utilization of pitch as a source of energy, efficient methods must be devised to reduce the sulfur content of the feedstock to acceptable levels. The major objective of this study is to establish the novel microwave catalytic processes in the hydrodesulfurization of pitch at low pressure and temperature. This novel approach was first developed at Queen's University for disposing toxic organic chemicals. The process involves a combination of effects of microwave irradiation (high electric field) and metal powder/metal hydride powder catalysts. The experimental work has been carried out as contract research by W & Y Consultants Kingston Ltd, at the Queen's University Laboratories. Special arrangements have been made with Professor R. D. Heyding to custom prepare a number of potentially effective metal hydrides to be used as the catalyst/hydrogen atom source. Characterization of these custom-prepared metal hydride was carried out in Professor Heyding's laboratory using x-ray powder diffraction technique.

The overall experimental work was organized into four parts. (1) To repeat previous experiments with metal powder and to develop a better method for the circulation of the gases within the reactor; (2) To prepare a number of new metal hydrides and to compare their effectiveness with the old metal powder experiments; (3) To develop better analytical techniques for the analysis of sulfur and for the determinations of the gaseous products in representative experiments; (4) To carry out some preliminary experiments with other materials, including gas-oil and bitumen and model compounds for the purpose of gaining some basic understanding of the processes. Preliminary data were also obtained from this study which showed the estimated costs of such a process in the commercial scale operations.

EXPERIMENTAL

1. The Microwave Radiation Sources

Previous study (DSS Contract Serial OSQ80-00152) employed a high-power 2 kW 2.4 GHz microwave magnetron source with an oven-type large cavity. In order to concentrate part of the dispersed microwave onto the reaction cell, a copper cell holder was used. In the current study, two additional microwave systems were assembled for specific purposes. They are described below.

(a) The design and contruction of an X-band resonant cavity system for high intensity microwave irradiation of chemicals. - The advantages of using an X-band source/cavity system include the higher polarization, higher oscillation frequency of the electric field (9.2 GHz in our system), and the good availability of commercial components at this band. Using a high Q commercial cavity, it is possible to produce a high intensity microwave field by use of a relatively weak power source. The feeding and monitoring systems are designed to provide an easy, well controlled operation of the system. Block diagram and schematics are shown in Fig. 1 and 2.

A custom electronic control box was built as the central unit of the overall system. The box contains electronic equipment to provide automatic frequency control (AFC), automatic level control and variable duty cycle pulse modulation of the powers. Different devices to allow monitoring of forward, reflected and transmitted power to and from the cavity as well as measurement of the Q-factor of the cavity are included.

The microwave source is a Hewlett Packard 8690B generator main frame with a HP 8694B X-band plug-in. The generator is followed by a Hughes H1117, 10W TWT microwave amplifier. The microwave energy is pulsed with variable duty cycle to provide a constant peak field strength in the cavity and allow variable heating of the sample at the same time. The pulse frequency is crystal controlled and is up to 1kHz to match our existing VSWR-meter. The commercial cylindrical cavity used is a Varian V4535 model with a 3 cm opening and it operates on only three

possible modes; TE_{011}, TE_{012}, and TE_{013}. The cavity was calibrated and its Q-factors were measured in our microwave chain and the typical results are given below in Table 1.

Table 1. Characterization of Varian Cavity operating in the Microwave System

MODE	Frequency	Q	Power	E-field
TE_{011}	9.073 GHz	37,000	13.6 W	181481 V/m
TE_{012}	9.836	3,850	12.3	0
TE_{013}	10.449	3,380	11.8	54631

It was surprising to us initially that the commercial cavity could achieve a Q nearthe theoretical value. The 37,000 value for the TE_{011} mode would indeed be most suitable and economical for our chemical studies. To simulate the chemical experimental conditions, a quartz tubing of 2.5 cm diameter was inserted into this cavity and a powder mixture of iron/pitch in 1:1 weight ratio was introduced into the centre of the cavity with the reaction cell mounted horizontally. The loaded Q under these conditions still measured to be greater than 8,000. This microwave system was used mainly for subsequent model compound study.

(b) The use of a low-power commercial microwave oven as the microwave source. - The above-mentioned cavity based microwave system is very costly, with a current price for the commercial cavity exceeding $8,000. It is, therefore, also desirable to test a cheap microwave source which might indeed be efficient in our metal hydride experiments. A 500 W 2.4 GHz Hitachi microwave oven was purchased with the inside of the oven lined with stainless steel. The two side walls of the oven were modified to allow access of pyrex tubings in and out for gas circulation. A custom

electronic control box was built to operate the pulse sequence of the microwave source. A digital meter was used to monitored the pulse width of the microwave irradiation. Because of the lower power available, the pulse width was stretched from 1 second to 5 seconds.

An on-line Gc/mass spectrometer was also interfaced with this system.

2. The Analytical Methods

(a) Sulfur analysis. - In previous studies, batch samples were sent out to another firm for C, H, and S elementary analyses. It was subsequently discovered that many of these outside analyses were not satisfactory. After confirming with the Queen's Chemical Engineering Department which had similar difficulties and experience with the same outside analyses, we had to developed our own standard S analysis, which can be controlled each time by a known standard calibration. The method we used is basically known as the oxygen flask combustion technique for micro-combustion analysis of sulfur.

The oxygen flask used was similar to a typical Erlenmeyer flask with the exception that there is a well surrounding the ground glass joint at the top of the flask. This well holds the absorbent liquid, which is 10 ml of distilled water and 10 drops of 30% hydrogen peroxide. Oxygen is introduced into the flask for a few minutes to flush out all the air in the flask. The sample is wrapped in a filter paper and then placed in the Pt basket before inserting into the flask and sealed tight. Approximately 20 minutes are allowed for a complete combustion and absorption. After combustion, 20 ml of distilled water, 30 ml of ethanol, 3 drops of 0.2% Thorin indicator and 1 drop of 0.01% methylene blue were added to the absorbent liquid and titrated against 0.0097 F barium perchlorate. The overall chemical reactions can be represented as the following:

$$\text{Organic sulfur} + O_2 = CO_2 + H_2O + SO_2 \; ; \; SO_2 + H_2O_2 = H_2SO_4$$

$$H_2SO_4 + Ba(ClO_4)_2 = BaSO_4 + 2\,HClO_4$$

This method was used on numerous standard systems and carried out by three different operators in the laboratory. The error of the analyses was established to be ± 0.6% under such varied conditions. The reproducibility within each sample was better than ± 0.5 %.

(b) Gas Chromatography. - A Hewlett Packard gas chromatograph was used for routine gas analysis. Provision was made so that the reaction cell, after microwave irradiation, could be attached to the 6-port valve of the chromatograph and the gas introduced into the column by opening the stopcock of the cell and operating the gas valve in a manner to fill the sample loop. A digital manometer was attached to the valve/sample loop system for quantitative sample measurements. Because of the nature of the gases to be analysed, we chose to use a thermal conductivity detector and either nitrogen or helium as carrier. The column used was packed with Porapak Q which is rather non-polar for the separation of hydrogen, carbon oxides, methane, ethane, hydrogen sulfide, etc. A typical operating condition sets the temperatures of the column and the detector at 50 and 200 ^{o}C, respectively. The carrier gas flow was in the range between 17 and 25 ml/minute.

(c) Mass Spectrometric Analysis. - Batch samples were analysed by Professor J.D. McCowan, using a simple AEI mass spectrometer.

(d) On-line Gc/Mass Spectrometer. - Towards the end of this project, we were able to construct a simple on-line Gc/mass spectrometer for direct analysis of the gaseous products. The Hewlett Packard gas chromatograph was modified to allow a slow leak into the ionization chamber of a quadrupole mass spectrometer. For simplicity in operating and compactness in space, we have chosen to use the Spectrum Scientific 1000D model quadruple mass spectrometer which can operate up to 100 mass number. Currently, we are assembling a microprocessor and some software to coordinate the gc and mass signals under rapid sweeping conditions. Two typical modes were used up to now. The first mode was to operate the mass spectrometer

as a fixed mass detector. A two-pen Hewlett Packard recorder was used to coordinate the gc peaks and the mass peaks at a fixed mass number. The second mode of operation was to use the internal ramp to sweep a small mass range (e.g. 2 mass units) at one second interval while the gc was operating.

(e) Preparation of Metal Hydrides. - The commercially available $LaNi_5H_6$ was provided to us by the National Research Council of Canada. All other intermetallic hydrides were prepared in Professor R.D. Heyding's laboratory. Three of these were chosen because they are more 'stable' at room temperature than the $LaNi_5H_6$ and more importantly, they are more economical. They are Mg_2NiH_4, $CaNi_5H_3$, and Mg_2CuH_x.

All hydrides were prepared in a stainless steel reactor system, shown in Fig. 3. The reactor temperature was controlled by an electrical furnace. Each metal alloy was grounded to -100 mesh and weighed before introduced into the reactor. The whole system was flushed with hydrogen and followed by evacuation during the heating of the reactor to the activation temperature. Hydrogen was then introduced into the reactor up to the necessary activation pressure (see Table 2). The formation of the hydride was first accompanied by a pressure drop in the reactor. The pressure was then maintained at the activation limit and the alloy was left to hydrogenate for at least 12 hours. After the reaction, the metal hydride was again weighed and its x-ray powder diffraction pattern was taken and compared with the pattern of the initial alloy. X-ray powder diffraction was done in Professor R.D. Heyding's laboratory using his Gdw type diffractometer.

Table 2. Hydriding Activation Temperatures and Pressures

Alloy	Temp. ^oC	Pressure kPa
Mg_2Ni	325	2100
$CaNi_5$	25	2100
Mg_2Cu	300	2400

While the identity of the hydrogen atoms sitting in the interstitial sites of the alloy can be confirmed by x-ray diffraction, the yield of the hydriding processes was simply obtained by weighing the products (Table 3).

Table 3. Weights of alloys after one hydriding cycle

Alloy	Wt. before, gm	Wt. after, gm
Mg_2Ni	1.109	1.148
$CaNi_5$	2.685	2.712
Mg_2Cu	1.587	1.635

RESULTS AND DISCUSSIONS

1. Hydrodesulfurization of Pitch with metal powder and conventional hydride with 2 kW microwave irradiation.

The earlier experiments in this project attempted to repeat some of the previous experiments using metal powder mixed with pitch. The typical experiment used 1 g of iron powder (-325 mesh), thoroughly mixed (grounded) with 1 g of pitch and placed in a 'fluidized cell' partioned with two sintered glass plates. Hydrogen was then circulated through the cell at 2 to 4 atmospheres. The temperature of the reaction cell was a function of the pulse rate and varied between room temperature and about 100 ^{o}C. At the end of the experiment, the sample was treated with toluene to dissolve most of the organic material, and the metal powder was separated from the solution by centrifuge. The residue pitch was then recovered from the solution and sent for sulfur analysis. The typical results are shown in Table 4.

Table 4. Analytical results of the microwave hydrodesulfurization of pitch using iron powder and 2 kW microwave source.

Sample	H_2, kPa	Pulse duration	S content	% S removed
1	230	4 sec (total of 120 sec)	3.80 %	33.3
2	230	5 sec	3.45 %	38.5
3	400	4 sec	3.0 %	47.3
4	150	4 sec	3.39 %	40.5
5	150	2 sec	3.73 %	34.5

In the above experiments, the result represents an average of three duplicate runs. There was not much a trend developed by varying the pressure or temperature. Furthermore, in two of the sample analyses which included carbon and hydrogen, a fairly unreasonable hydrogen to carbon ratio was obtained. (C, 76.5%, H, 7.12 %). Initially, it was thought that the pitch was being hydrogenated which might be competing with the hydrodesulfurization process. A standard check of the analytical results showed that the carbon was indeed inaccurate. At this point, we have assumed all sulfur analysis in our own laboratory using the oxygen flask method.

In the 'fluidizing' experiments, an additional difficulty was encountered. To enhance the fluidization, positive pressure was applied vertically against the particles laying on the surface of the sintered glass plate. When the particles came down, the pitch and the metal powder were inadvertently separated which would decrease the reaction efficiency. This approach was therefore discarded.

Another series of experiments were carried out using a mixed iron powder and $LiAlH_4$ powder as the catalyst. The reaction was performed in an ordinary pyrex cell under an atmospheric pressure of hydrogen. A liquid nitrogen cold trap was installed on the same line as the reaction cell but outside the microwave oven

to achieve some degree of circulation via a large temperature gradient. The experimental parameters such as pressure and temperature were again varied as before. The sulfur analyses were performed immediately in our laboratory, each time compared with a standard untreated pitch sample. For the untreated pitch, our analytical results gave an average of 6.5 $\pm$ 0.05% of sulfur. The results of this series of experiments are given in Table 5.

Table 5. Analytical results of the microwave hydrodesulfurization of pitch using Fe/$LiAlH_4$ mixed catalyst and 2 kW microwave.

Sample	H_2, kPa	Pulse duration	S content	% S removed
0		untreated pitch standard	6.50	
1	150	3 sec (total of 120 sec)	3.20	50.7
2	230	3 sec	3.08	52.6
3	400	3 sec	2.14	67.0
4	400	4 sec	2.08	68.0
5*	400	4 sec	2.01	69.0

Again, each sample result is the average of three duplicate runs. In sample 5, the sample was allowed to equilibrate with hydrogen at 400 kPa for 3 hours before microwave irradiation. The difference observed between samples 4 and 5 is not considered to be significant. What is significant is that the increase of hydrogen pressure and the mixing of $LiAlH_4$ with Fe powder definitely improves the efficiency of desulfurization. There is no doubt that we have not yet been able to reach an optimum design for the reactor cell and the circulation of the gases.

Another experiment was performed using nickel powder (-325 mesh) and $LiAlH_4$ in a 1:1 mixture as catalyst. All other conditions were identical to the sample run #4. The result was identical. The use of $LiAlH_4$ seemed to improve the final percentage of sulfur removal, but it did not lower the requirements of time and power (i.e. energy). Furthermore, an experiment was performed using $LiAlH_4$ only as the catalyst and the result showed only 20 % removal of sulfur. It was thought that the conventional $LiAlH_4$ serves only as a source of hydrogen and that the surface probably lacks the same activity as iron or nickel. Subsequently, we have prepared other alloys containing nickel or copper and hydrided to serve both as source for hydrogen and to provide the catalytic surface. These metal hydride experiments will be described in the next section.

At this point, we wish to make some comments on the sulfur analyses performed in our laboratory. Upon extensive and careful examination, we found that a small contribution of sulfur in our analyses came from the particular type of filter paper we used during the combustion process. A series of blank runs using the filter paper only showed a percentage of 0.6 % by weight. Since our major goal is to monitor the 'relative' percentage of sulfur removal after the microwave process, and that all our analytical procedures were standardized (using the same stock of solutions, paper, etc.), we conclude that the procedure and the results are satisfactory.

2. Hydrodesulfurization of Pitch with metal hydride powder and microwave radiation.

The first series of metal hydride experiments was performed using the $LaNi_5$ alloys provided by NRCC. This alloy hydride has a dissociation pressure of about 200 kPa at room temperature. The samples we used were only partly hydrided, as shown by x-ray powder diffraction. The samples were mixed with pitch (0.5ghydride to 1 g pitch and 1 g nickel) in a glove box under 230 kPa pressure of hydrogen. The reaction cell was then sealed off by shutting the stopcock and then placed in the 2 kW microwave oven for irradiation. The initial experiments using normal irradiation time resulted in violent explosion. Radiation time was therefore

substantially reduced to atotal of only 10 seconds with a pulse duration of 2 sec. This amount of energy was sufficient to remove again about the same amount of sulfur from the pitch, i.e. about 68 %. After the short microwave irradiation and before opening the reaction cell, we could observe the presence of some yellow form of sulfur condensing on part of the wall of the cell. The gaseous products were subsequently examined by mass spectrometry and gas chromatography. The use of $LaNi_5$ imposed some handling problems, as the samples had to be mixed in a glove box. In order to eliminate this problems, other alloys were used and they were chosen for their low dissociation pressure when the hydrides were formed. Three of these were prepared and two were used for the hydrodesulfurization experiments. The results are given in Table 6.

Table 6. Analytical results of the microwave hydrodesulfurization of pitch using metal hydrides and 2 kW microwave power.

Sample	Hydrided Alloys	H_2, kPa	Pulse duration	S content	% S removed
1	$LaNi_5$	200	2 sec (total of 10 sec)	2.08	68.0
2	Mg_2Ni	100	2 sec (total of 10 sec)	3.21	50.6
3	Mg_2Ni	100	2 sec (total of 60 sec)	2.01	69.0
4	$CaNi_5$	100	2 sec (total of 10 sec)	3.15	51.5
5	$CaNi_5$	100	2 sec (total of 60 sec)	2.35	63.8

Each sample result is the average of three duplicate runs in a series. The metal hydrides used were examined by x-ray diffraction before and after microwave processes. The diffraction results showed that for all of our samples, only partial hydridization had been achieved (estimated at about 50%). After the processes, the extent of hydridization was substantially lowered but there was no significant

alternation of the alloy surface. Thus, it is safe to conclude that the alloys can be used again for hydridization and for microwave hydrodesulfurization.

The metal hydride experiments point to a significant conclusion: the reaction is much faster and the energy required is much less. The variation between different metal alloys may only be artificial, as we did not have a full control of the extent of the hydridization in each type of alloys. However, we should point out that of the three metal hydrides used, $LaNi_5$ is the least stable and $CaNi_5$ is the most stable with a dissociation pressure of only 5 Pa at room temperature. The use of metal hydrides also did not seem to drastically improve the total percentage of sulfur removed. That probably is again a reactor design problem. Here, we are dealing with two different parameters: the speed (or the effectiveness) of the reaction; and the extent of the completion of the reaction. It is also very likely that some of the sulfur in pitch is so strongly bonded that it is not easily removed by chemical processes. Further work on metal hydrides will continue.

3. Investigation of the gaseous products in the microwave metal hydride hydrodesulfurization of pitch.

Early investigations relied upon batch sampling techniques. The reaction cell was opened after the microwave irradiation to fill a sample loop for separate gas chromatographic and mass spectrometric analyses. The major products detected included methane, carbon dioxide, ethane, hydrogen sulfideand possibly some propane. No aromatic or unsaturated hydrocarbons were detected. An attempt of quantifying the amount of hydrogen sulfidewas abandoned for two reasons: the correlation would be very poor, as elemental sulfur is one of the reaction products; and the fact that hydrogen sulfidesensitivity is very poor on our Porapak Q column. Table 7 lists the gaseous components identified by Gc and separately by mass spectrometry in some typical experiments. A typical gas chromatogram of the results

is given in Fig. 4.

Table 7. Identifications of Gaseous Products by Gc and by Mass spectrometry in the microwave hydrodesulfurization.

Sample	System	Gaseous Products	Remarks
5-4	Pitch/Fe/$LiAlH_4$	CH_4; H_2S; CO_2	Small quantites
6-1	Pitch/$LaNi_5$-Ni	CH_4; CO_2; C_2H_6; H_2S; C_3H_8	Large methane peak; in one of the 3 runs ethane peak was about 30% of the methane peak.
6-3	Pitch/Mg_2Ni	CH_4; CO_2; C_2H_6; H_2S	Large methane peak.
6-5	Pitch/$CaNi_5$	CH_4: CO_2; C_2H_6; H_2S	Large methane peak.

Towards the end of this project, we were able to construct a simple on-line Gc/Mass spect analytical apparatus for gas analysis. Because this is a low-cost home-made facility, substantial labour and expertise had to be invested to bring the performance up to a satisfactory level. Currently, we are staisfied with the Gc/Mass spect performance as we have had extensive test of the instrument in determining hydrogen isotope distributions in hydrocarbons. A typical Gc/Mass spect result on the methane product is shown in Fig. 5.

The abundant production of methane in the microwave processes is not surprising. The presence of ethane and propane would be a bonus, and it may be possible to produce higher hydrocarbons later. Much work is needed on the gas product study before any major conclusion is significant. The current results, however, suggest that pitch can also be gasified as an alternative to direct combustion.

4. Preliminary Experiments on microwave hydrodesulfurization of other organic materials.

The application of this process to some bitumen samples and some gas-oil products (provided by Dr. J. Kriz) was briefly carried out. There was some difficulty in handling the mixing of the bitumen with the metal and metal hydride. A typical experiment used 1 g of mixture of Ni and $LaNi_5$ (1:1 ratio by weight) and an unweighed portion of bitumen and gas-oil. The sample was mixed in a glove box and the reaction cell as sealed off. The sample was subject to 2 kW microwave irradiation for a total of 10 seconds with 2 sec pulses. Our analyses of the untreated bitumen gave a sulfur content of 6.2% by weight. After the microwave treatment, the bitumen recovered had a sulfur content of 3.2%. Mass spectrometric analyses of the gaseous products showed the presence of methane, ethane, and hydrogen sulfide; all were in smaller quantities as compared to the same pitch experiment. These results are reproducible in duplicate runs with the sulfur content after treatment ranged between 3.2% and 3.41%. The preliminary results with the bitumen indicate that the reaction does proceed but it does not proceed readily to completion. The mixing problem in the bitumen sample certainly would be more severe than in the pitch case.

Exactly the same experiments were done using the gas-oil. A different problem was encountered in this case, as the density of metal/metal hydride is so much larger than the gas-oil. Mixing again is very inefficient and therefore no qantitative analyses were made.

5. Preliminary Experiments using the cavity based X-band microwave system.

The advantages of using a laboratory cavity based microwave system include the precise measurement of energy input into the sample. Using a very high Q commercial cavity, it appears to be possible to carry out chemical experiments with a low power microwave source. The experiments were performed using a model

compound, thianthrene, ($C_{12}H_8S_2$, S content = 29.6% theoretical, 30.05% found).

A typical experiment used 0.5 g of thianthrene thoroughly mixed with 0.5 g of nickel powder (-325 mesh). The sample was placed in a quartz tubing of 2.5 cm diameter and the tube was inserted into the X-band cavity. The resonant cavity was tuned in the TE_{103} mode. The sample tube was first evacuated and then filled with hydrogen at 150 kPa pressure. Precisely 6.50 watt of microwave power at 10.4 GHz was introduced into the cavity and the reaction cell. The microwave was introduced in the pulsed mode and the total irradiation time was 120 seconds. The results of a series of such experiments are given in Table 8.

Table 8. Microwave hydrodesulfurization of thianthrene in a cavity based X-band microwave system.

Sample	Composition	Power in-put	Time	S content	% S removed
1	0.5 g thianthrene/ 0.5 g nickel	6.50 watt	120 sec	24.9	15.8
2	0.5 g thianthrene/ 0.5 g nickel	8.80 watt	120 sec	25.6	13.5
3	0.5 g thianthrene/ 0.5 g nickel	6.50 watt	300 sec	24.5	17.2

The results included duplicated runs under the same conditions. Although these experiments can only be considered as preliminary, some significant conclusions are indeed apparent. With a high Q cavity, even a low power below 10 watt level can achieve a sufficiently high electric field to induce the processes. The experimental difficulty lies in the arrangements of the sample in the exact position of the cavity where the field is at a maximum. For example, the maximum field occurs at the centre of the cavity and along an axis of about 4 cm in length. Our reaction cell is 2.5 cm in diameter and about 7 cm in length. Most of the sample

actually lay at the bottom of the tube, [redacted] away from the maximum centre field. As the sample had to be spreaded along the tube, a portion of the sample was therefore not even in the active part of the cavity. Nevertheless, the reaction did produce a significant amount of desulfurization, although in terms of percentage it was far from completion. It would be worthwhile to follow up on some of these model experiments.

6. Preliminary estimate of the energy balance in the microwave hydrodesulfurization processes.

A number of assumptions are made to estimate the order of magnitude of the energy in the microwave hydrodesulfurization processes. The first one states that the generation of microwave energy by electricity is about 50% efficient. The second assumption states that only part of the microwave energy is utilized due to the geometry of the sample arrangements. We shall start with the model cavity based system in which the power input can be accurately controlled and measured.

In a typical cavity experiment, 6.5 watt of microwave power was applied to the cavity for a total duration of 120 seconds. Thus, a maximum of 2.2×10^{-4} kWh (killowatt-hour) of energy was consumed. The typical sulfur removed in such an experiment was 0.023 g. Assuming a 50% utilization of the incoming microwave power for the chemical processes, a 'raw' electricity supply of 2.2×10^{-4} kWh again was required. For a linear projection, 1 kWh of electricity will remove 100 g of sulfur from thianthrene.

In a typical pitch experiment, a similar calculation gives the requirement of 5×10^{-3} kWh of electricity for the removal of 0.044 g of sulfur. In the pitch experiment where the oven cavity is much greater than the reaction cell, the estimate of 50% utilization of microwave power would be too high but it would serve as an upper limit of the energy consumption. Therefore, the highest estimate for the process is that 5 kWh of electricity is used to treat 1 kg of pitch to reduce the

sulfur content from 6 to 2 %.

The cost of energy in such a treatment, at an upper limit is fairly high. Considerations must then be taken into accounts the amounts of gaseous fuel (such as methane, ethane) as a by product of the processes. The requirement of the hydrogen source will increase the cost still further, but in a separate study, we are able to demonstrate that hydrogen can be produced in good yield by adding water into the system, and irradiated in a low-power commercial microwave oven for one or two minutes.

CONCLUSIONS AND SUGGESTIONS

1. It is concluded that under the laboratory testing conditions the use of certain metal hydride in the microwave catalytic hydrodesulfurization of pitch was more efficient than the use of metal powder.

2. An optimum level of up to 70% sulfur removal appears to be the limit of the current experiments. Serious design problems still remain unsolved. It is hope that further refinement in the reactor design will improve the overall efficiency.

3. The use of metal hydride also causes significant hydrogasification of pitch under laboratory conditions. The major gaseous hydrocarbons identified are methane, and ethane. Propane is also found.

4. Model experiments using laboratory precision apparatus, including a high Q cavity and and X-band stable microwave source at low power indicate that with suitable design the energy consumption can be reduced by more than 50% as compared to high power experiments.

5. Current efforts must be concentrated in the engineering designs of the whole microwave system, including the maximum use of power and maximum exposure of active surface to the microwave power. Continuing studies of metal hydrides are also required.

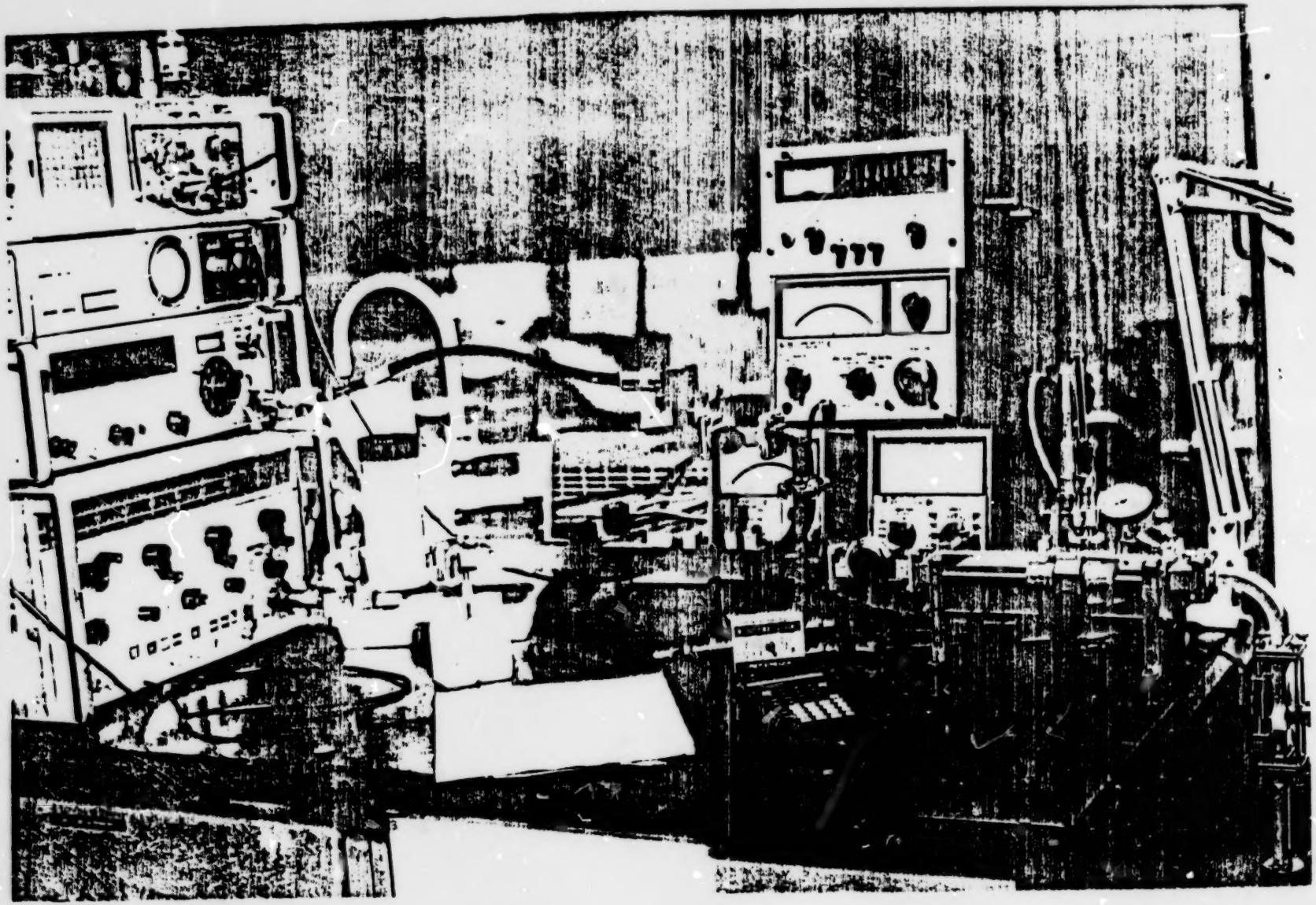

Fig. 1. A picture of the laboratory X-band microwave system.

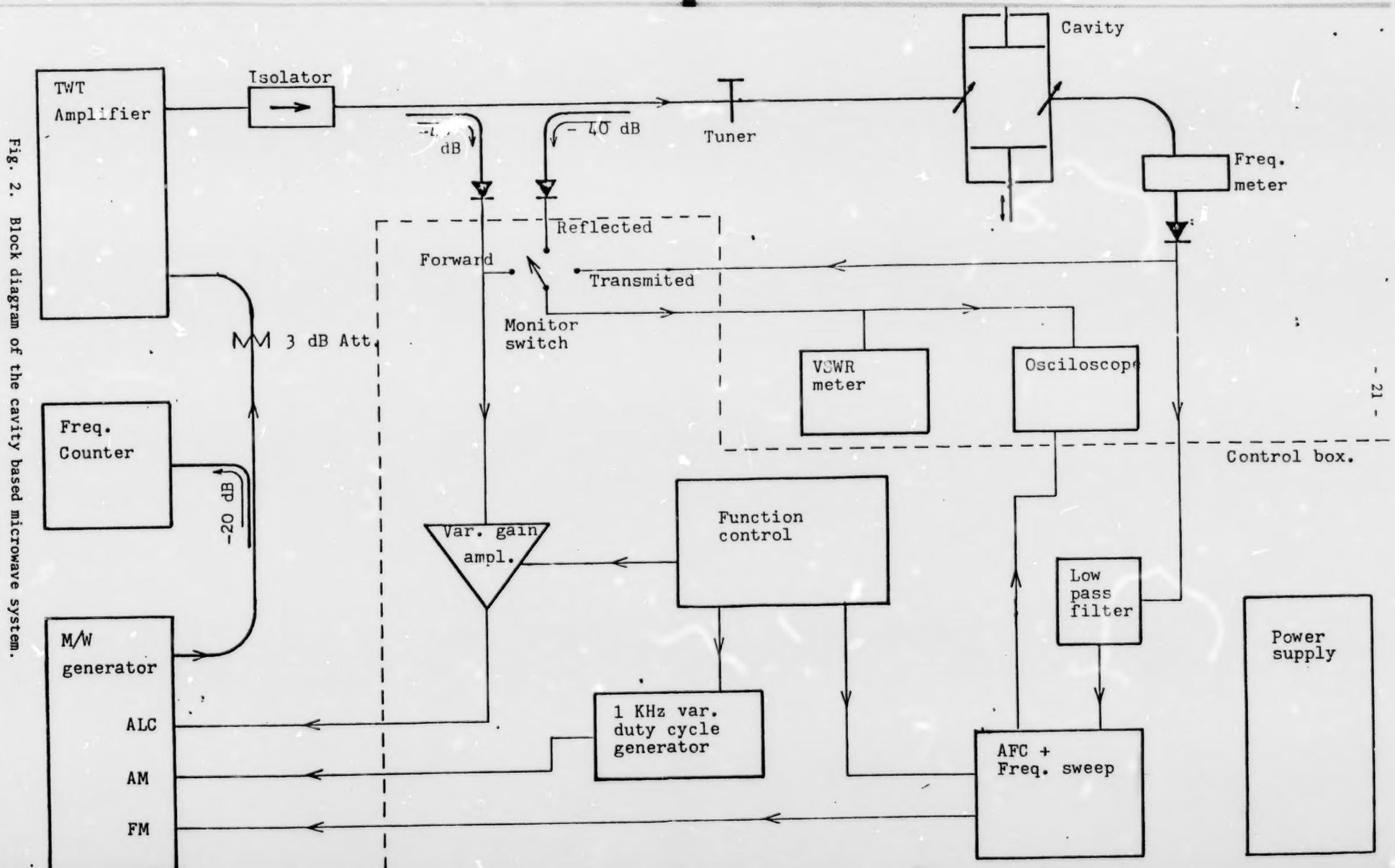

Fig. 2. Block diagram of the cavity based microwave system.

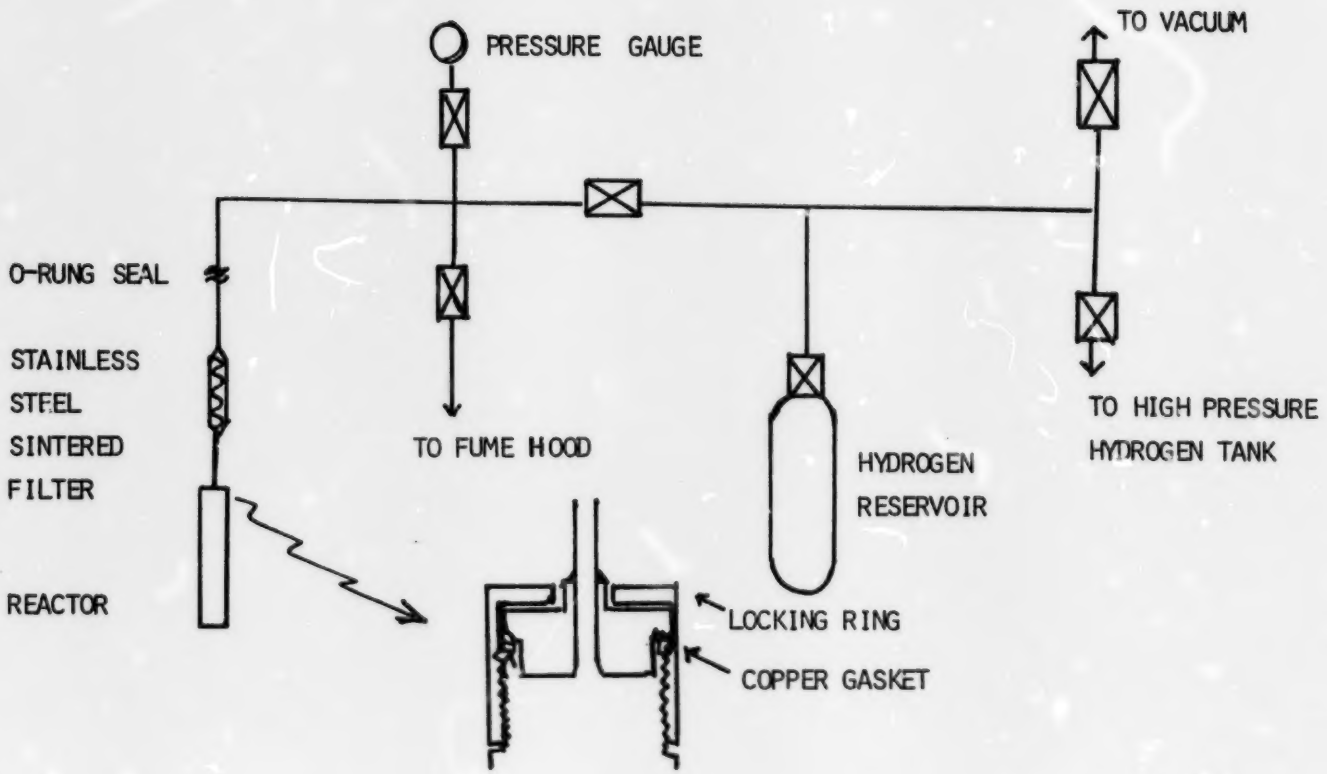

Fig. 3 Schematic presentation of the metal hydriding apparatus. Inset shows the details of the connector of the reactor.

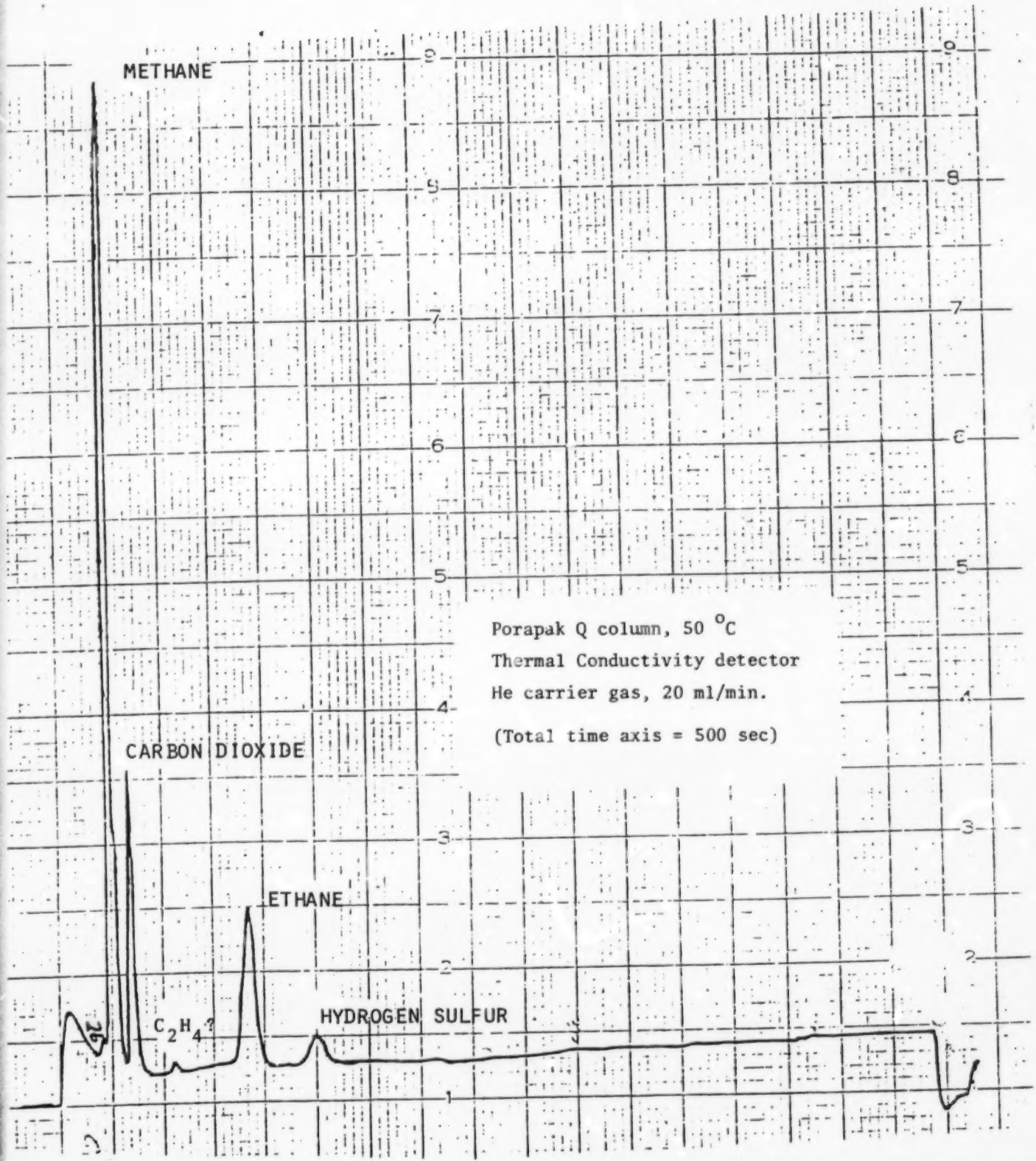

Fig. 4. A typical gas chromatograph analysis of the gaseous products in the microwave desulfurization of pitch with $CaNi_5$.

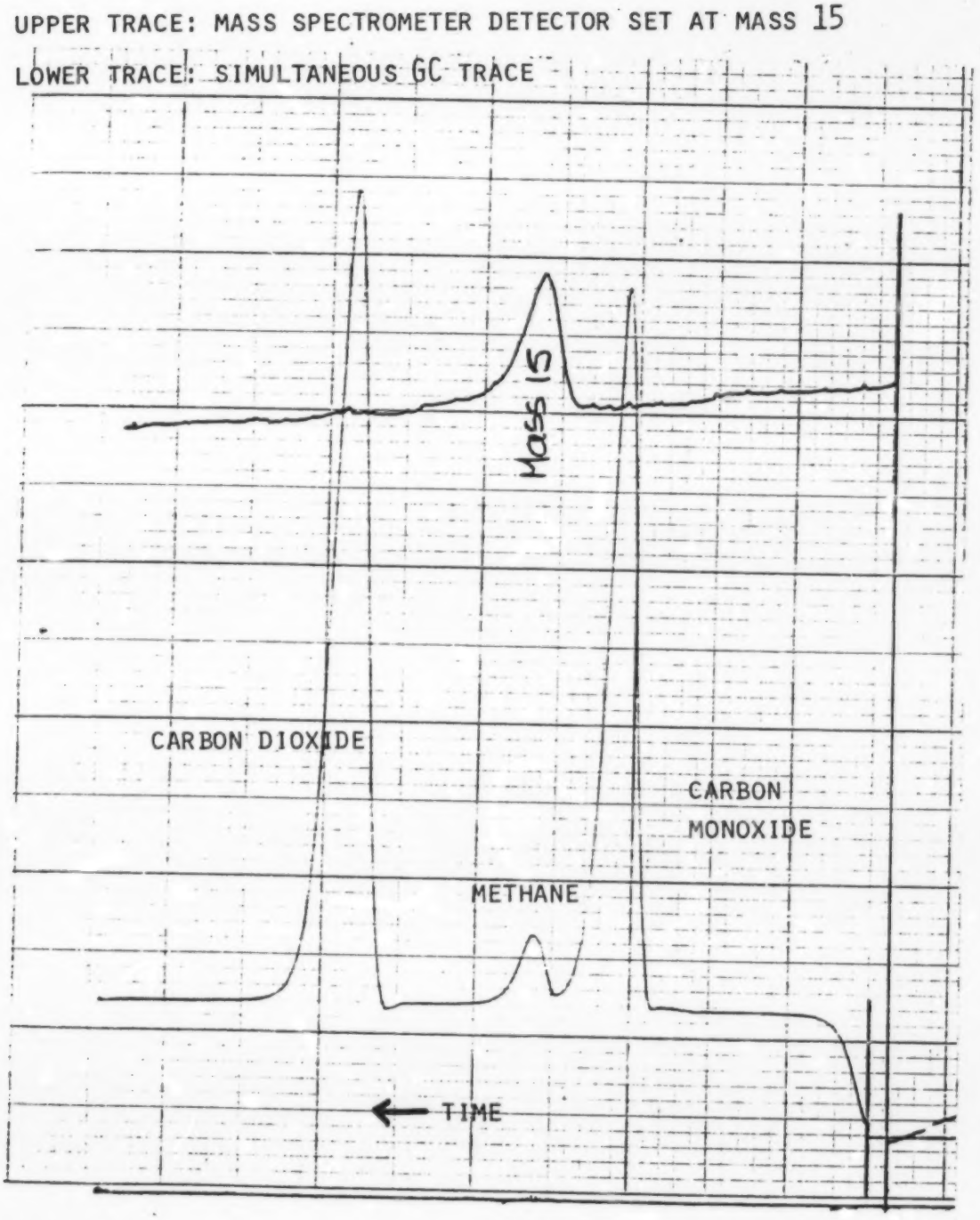

Fig. 5. A two-pen (two traces) recording of the Gc/Mass spect analysis of a sample containing CO, CH_4 and CO_2, from the microwave irradiation of a sample of $Ni/H_2O/CO$.